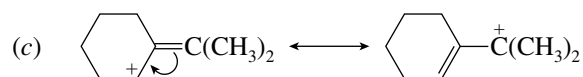
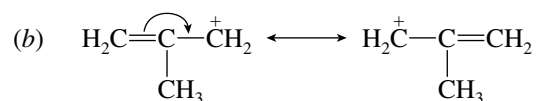


CHAPTER 10

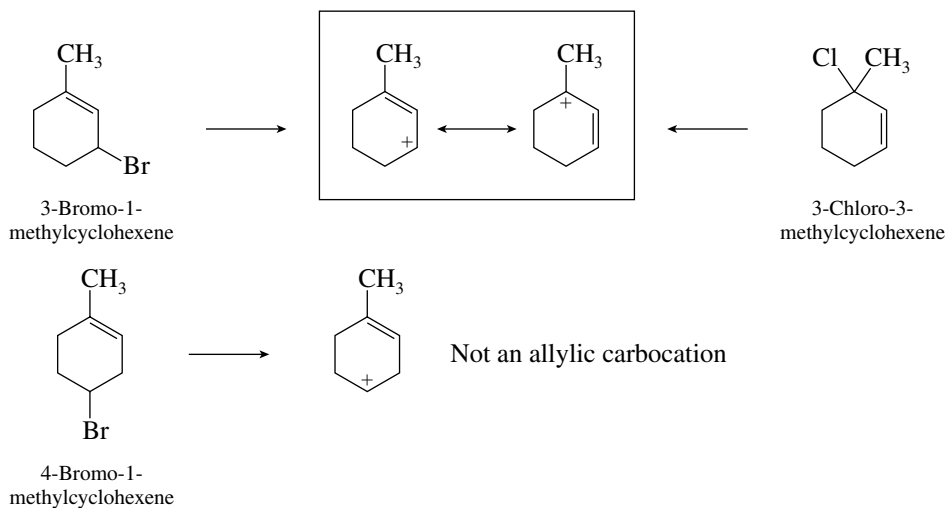
CONJUGATION IN ALKADIENES AND ALLYLIC SYSTEMS

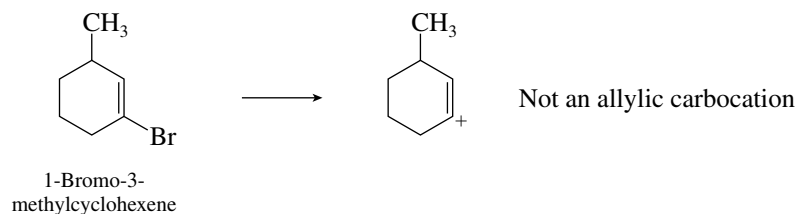
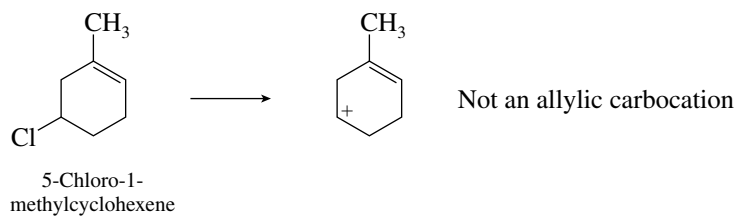
SOLUTIONS TO TEXT PROBLEMS

10.1 As noted in the sample solution to part (a), a pair of electrons is moved from the double bond toward the positively charged carbon.

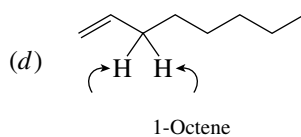
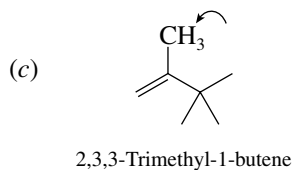
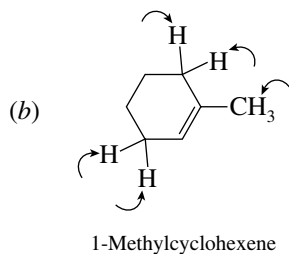


10.2 For two isomeric halides to yield the same carbocation on ionization, they must have the same carbon skeleton. They may have their leaving group at a different location, but the carbocations must become equivalent by allylic resonance.

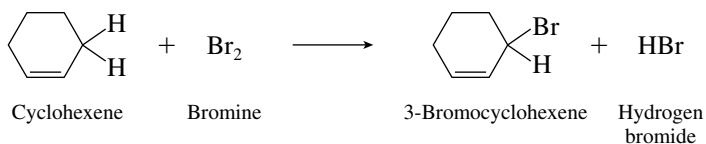




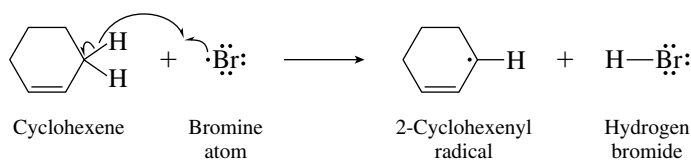
10.3 The allylic hydrogens are the ones shown in the structural formulas.



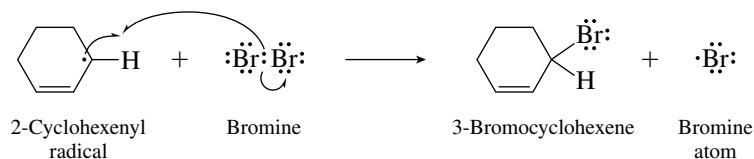
10.4 The statement of the problem specifies that in allylic brominations using *N*-bromosuccinimide the active reagent is Br_2 . Thus, the equation for the overall reaction is



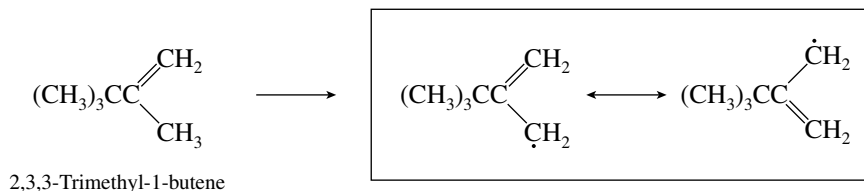
The propagation steps are analogous to those of other free-radical brominations. An allylic hydrogen is removed by a bromine atom in the first step.



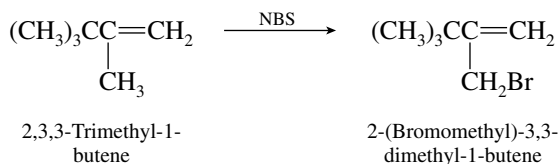
The allylic radical formed in the first step abstracts a bromine atom from Br_2 in the second propagation step.



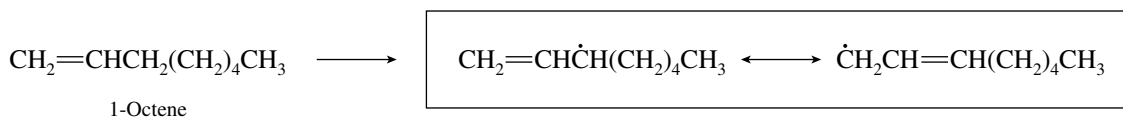
- 10.5** Write both resonance forms of the allylic radicals produced by hydrogen atom abstraction from the alkene.



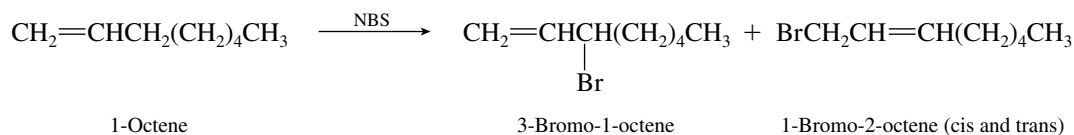
Both resonance forms are equivalent, and so 2,3,3-trimethyl-1-butene gives a single bromide on treatment with *N*-bromosuccinimide (NBS).



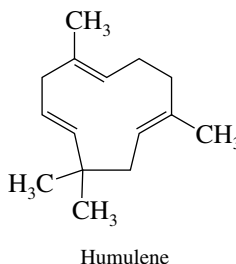
Hydrogen atom abstraction from 1-octene gives a radical in which the unpaired electron is delocalized between two nonequivalent positions.



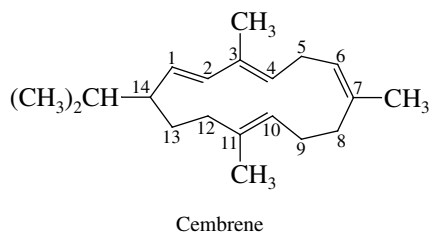
Allylic bromination of 1-octene gives a mixture of products



- 10.6** (b) All the double bonds in humulene are isolated, because they are separated from each other by one or more sp^3 carbon atoms.

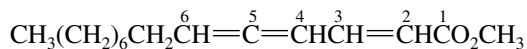


- (c) The C-1 and C-3 double bonds of cembrene are conjugated with each other.

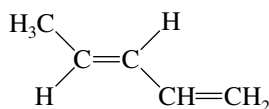


The double bonds at C-6 and C-10 are isolated from each other and from the conjugated diene system.

- (d) The sex attractant of the dried-bean beetle has a cumulated diene system involving C-4, C-5, and C-6. This allenic system is conjugated with the C-2 double bond.



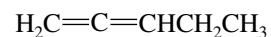
- 10.7** The more stable the isomer, the lower its heat of combustion. The conjugated diene is the most stable and has the lowest heat of combustion. The cumulated diene is the least stable and has the highest heat of combustion.



(*E*)-1,3-Pentadiene
Most stable
3186 kJ/mol
(761.6 kcal/mol)

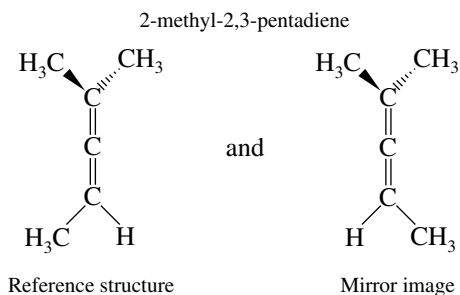


1,4-Pentadiene
3217 kJ/mol
(768.9 kcal/mol)

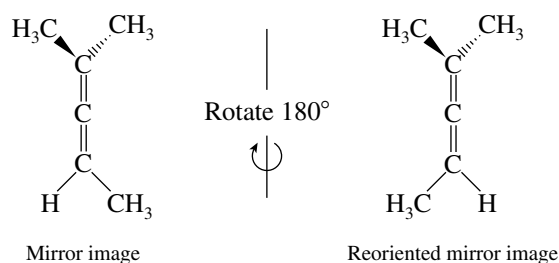


1,2-Pentadiene
Least stable
3251 kJ/mol
(777.1 kcal/mol)

- 10.8** Compare the mirror-image forms of each compound for superposability. For 2-methyl-2,3-pentadiene,

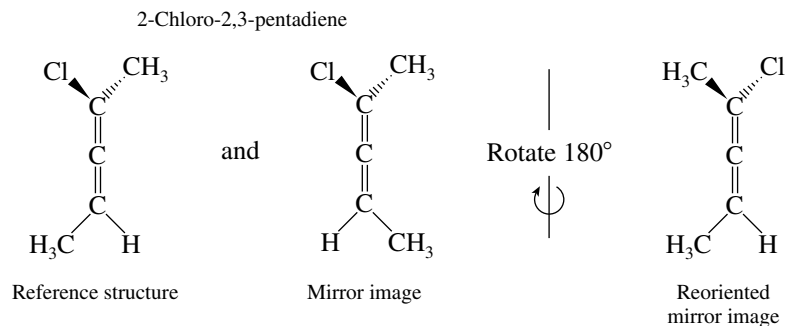


Rotation of the mirror image 180° around an axis passing through the three carbons of the C=C=C unit demonstrates that the reference structure and its mirror image are superposable.

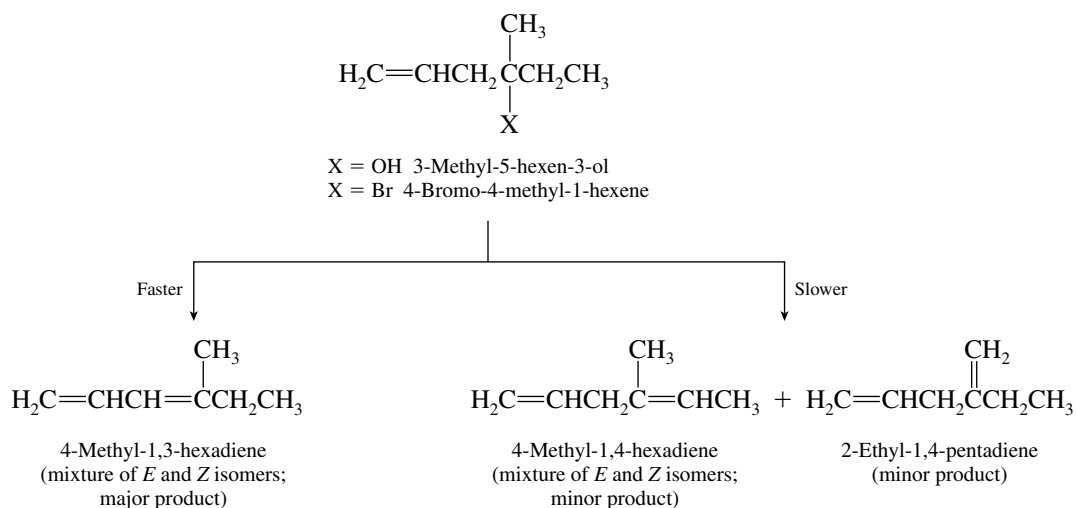


2-Methyl-2,3-pentadiene is an achiral allene.

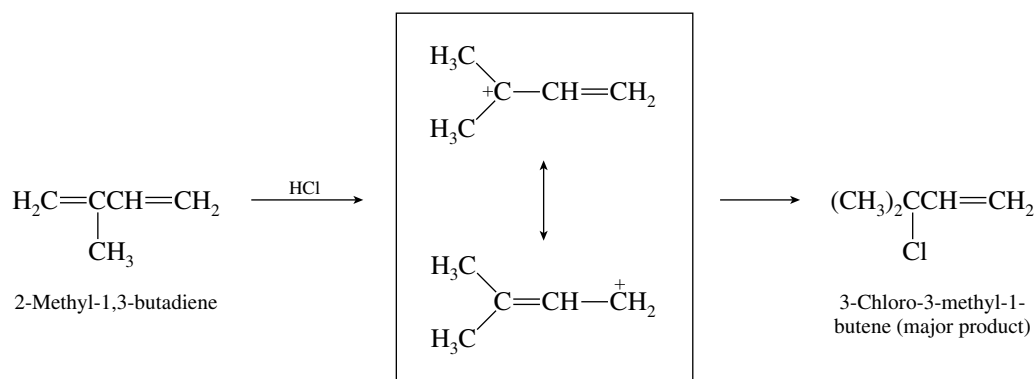
Comparison of the mirror-image forms of 2-chloro-2,3-pentadiene reveals that they are not superposable. 2-Chloro-2,3-pentadiene is a chiral allene.



- 10.9** Both starting materials undergo β -elimination to give a conjugated diene system. Two minor products result, both of which have isolated double bonds.

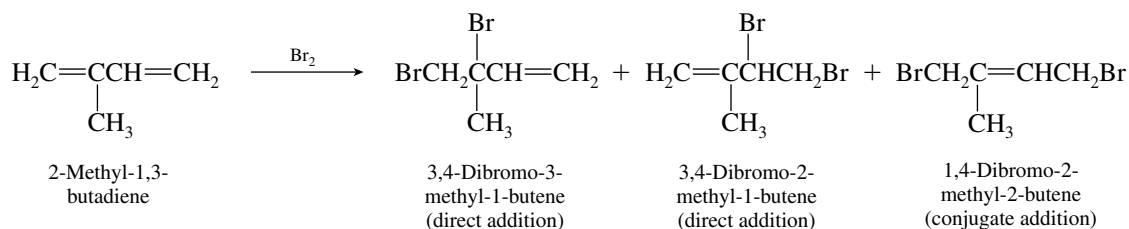


- 10.10** The best approach is to work through this reaction mechanistically. Addition of hydrogen halides always proceeds by protonation of one of the terminal carbons of the diene system. Protonation of C-1 gives an allylic cation for which the most stable resonance form is a tertiary carbocation. Protonation of C-4 would give a less stable allylic carbocation for which the most stable resonance form is a secondary carbocation.

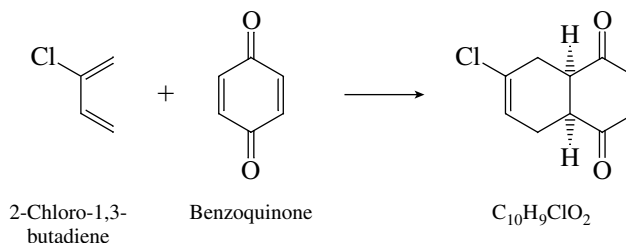


Under kinetically controlled conditions the carbocation is captured at the carbon that bears the greatest share of positive charge, and the product is the tertiary chloride.

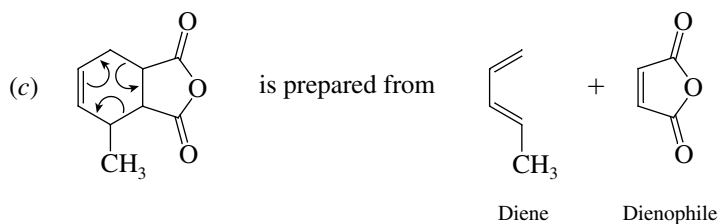
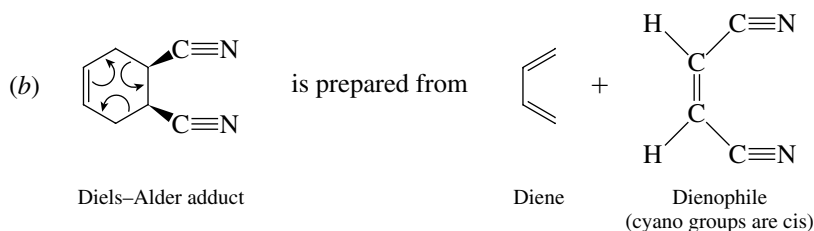
- 10.11** The two double bonds of 2-methyl-1,3-butadiene are not equivalent, and so two different products of direct addition are possible, along with one conjugate addition product.



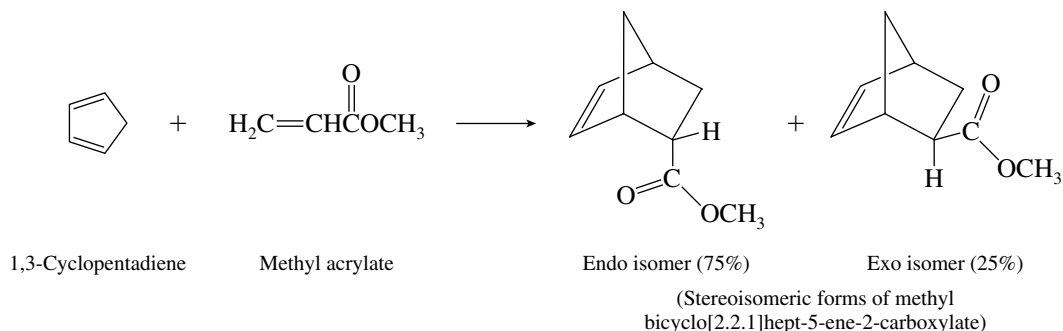
- 10.12** The molecular formula of the product, $\text{C}_{10}\text{H}_9\text{ClO}_2$, is that of a 1:1 Diels–Alder adduct between 2-chloro-1,3-butadiene and benzoquinone.



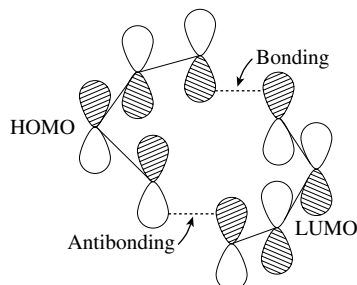
- 10.13** “Unravel” the Diels–Alder adduct as described in the sample solution to part (a).



- 10.14** Two stereoisomeric Diels–Alder adducts are possible from the reaction of 1,3-cyclopentadiene and methyl acrylate. In one stereoisomer the CO_2CH_3 group is syn to the $\text{HC}=\text{CH}$ bridge, and is called the *endo* isomer. In the other stereoisomer the CO_2CH_3 group is anti to the $\text{HC}=\text{CH}$ bridge and is called the *exo* isomer.

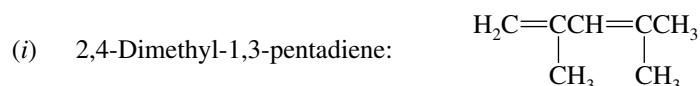
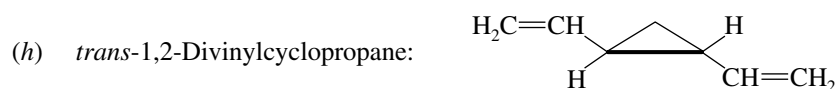
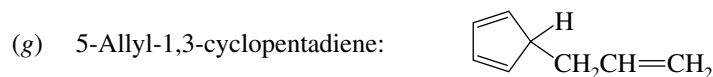
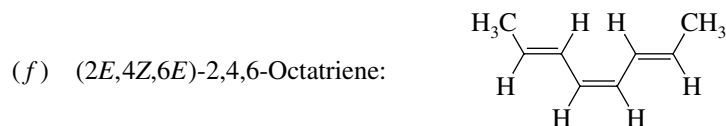
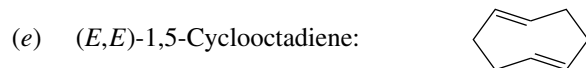
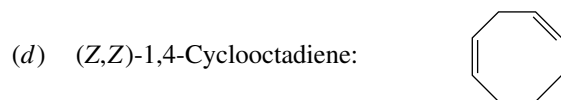
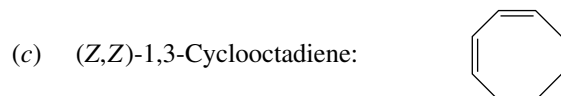
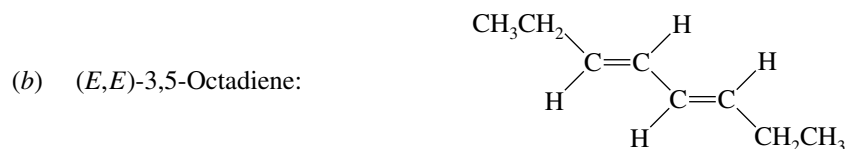


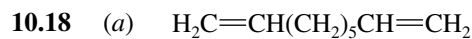
- 10.15** An electrophile is by definition an *electron-seeker*. When an electrophile attacks ethylene, it interacts with the π orbital because this is the orbital that contains electrons. The π^* orbital of ethylene is unoccupied.
- 10.16** Analyze the reaction of two butadiene molecules by the Woodward–Hoffmann rules by examining the symmetry properties of the highest occupied molecular orbital (HOMO) of one diene and the lowest unoccupied molecular orbital (LUMO) of the other.



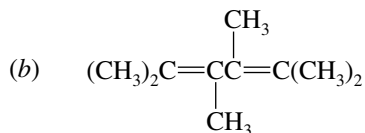
This reaction is forbidden by the Woodward–Hoffmann rules. Both interactions involving the ends of the dienes need to be bonding for concerted cycloaddition to take place. Here, one is bonding and the other is antibonding.

- 10.17** Dienes and trienes are named according to the IUPAC convention by replacing the *-ane* ending of the alkane with *-adiene* or *-atriene* and locating the positions of the double bonds by number. The stereoisomers are identified as *E* or *Z* according to the rules established in Chapter 5.

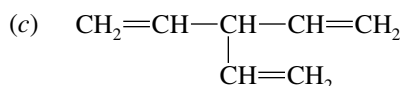




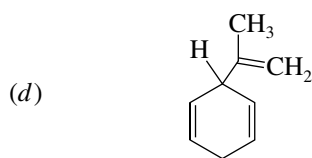
1,8-Nonadiene



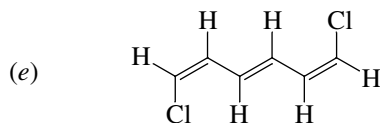
2,3,4,5-Tetramethyl-2,4-hexadiene



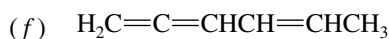
3-Vinyl-1,4-pentadiene



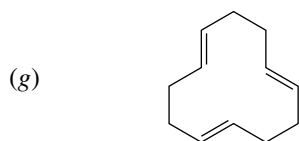
3-Isopropenyl-1,4-cyclohexadiene



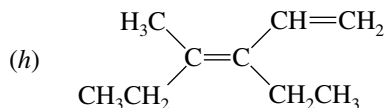
(1Z,3E,5Z)-1,6-Dichloro-1,3,5-hexatriene



1,2,4-Hexatriene

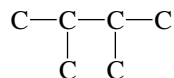


(1E,5E,9E)-1,5,9-Cyclododecatriene

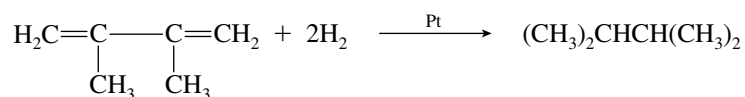


(E)-3-Ethyl-4-methyl-1,3-hexadiene

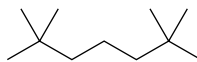
- 10.19 (a) Since the product is 2,3-dimethylbutane we know that the carbon skeleton of the starting material must be



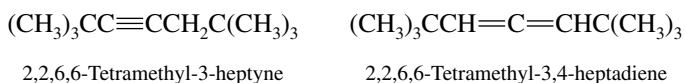
Since 2,3-dimethylbutane is C_6H_{14} and the starting material is C_6H_{10} , two molecules of H_2 must have been taken up and the starting material must have two double bonds. The starting material can only be 2,3-dimethyl-1,3-butadiene.



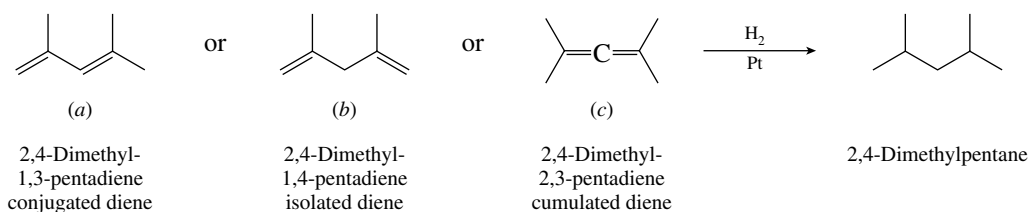
- (b) Write the carbon skeleton corresponding to 2,2,6,6-tetramethylheptane.



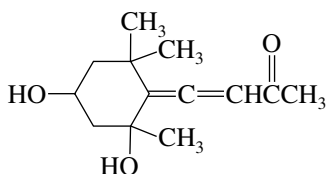
Compounds of molecular formula $C_{11}H_{20}$ have two double bonds or one triple bond. The only compounds with the proper carbon skeleton are the alkyne and the allene shown.



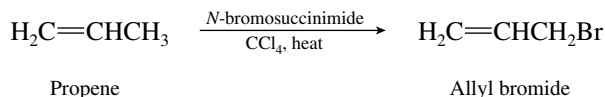
- 10.20 The dienes that give 2,4-dimethylpentane on catalytic hydrogenation must have the same carbon skeleton as that alkane.



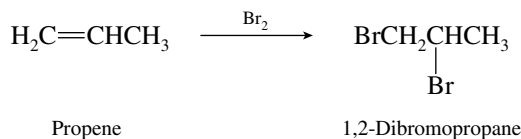
- 10.21 The important piece of information that allows us to complete the structure properly is that the ant repellent is an *allenic* substance. The allenic unit cannot be incorporated into the ring, because the three carbons must be collinear. The only possible constitution is therefore



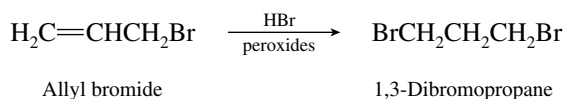
- 10.22 (a) Allylic halogenation of propene with *N*-bromosuccinimide gives allyl bromide.



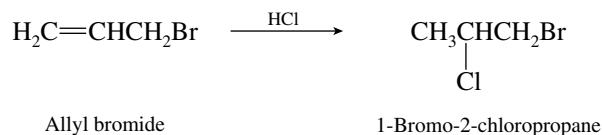
- (b) Electrophilic addition of bromine to the double bond of propene gives 1,2-dibromopropane.



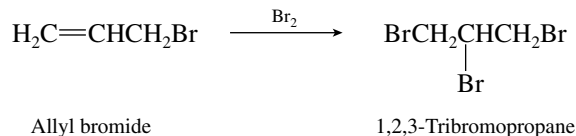
- (c) 1,3-Dibromopropane is made from allyl bromide from part (a) by free-radical addition of hydrogen bromide.



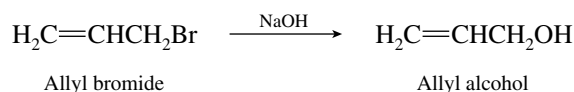
- (d) Addition of hydrogen chloride to allyl bromide proceeds in accordance with Markovnikov's rule.



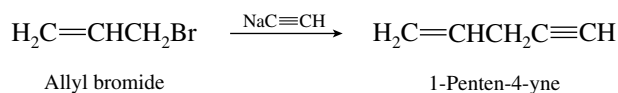
- (e) Addition of bromine to allyl bromide gives 1,2,3-tribromopropane.



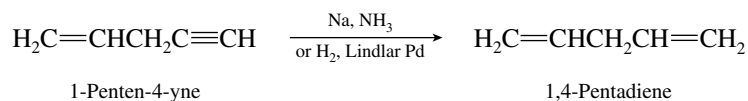
- (f) Nucleophilic substitution by hydroxide on allyl bromide gives allyl alcohol.



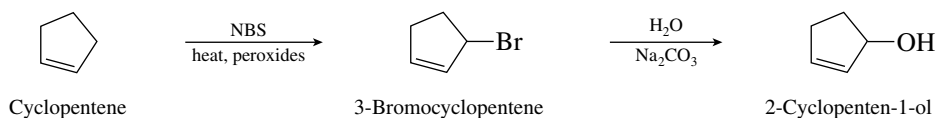
- (g) Alkylation of sodium acetylide using allyl bromide gives the desired 1-penten-4-yne.



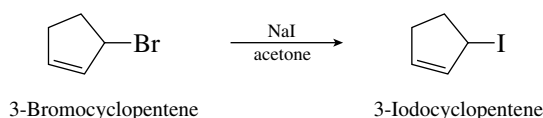
- (h) Sodium–ammonia reduction of 1-penten-4-yne reduces the triple bond but leaves the double bond intact. Hydrogenation over Lindlar palladium could also be used.



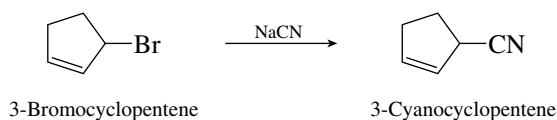
- 10.23** (a) The desired allylic alcohol can be prepared by hydrolysis of an allylic halide. Cyclopentene can be converted to an allylic bromide by free-radical bromination with *N*-bromosuccinimide (NBS).



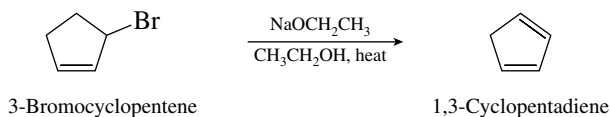
- (b) Reaction of the allylic bromide from part (a) with sodium iodide in acetone converts it to the corresponding iodide.



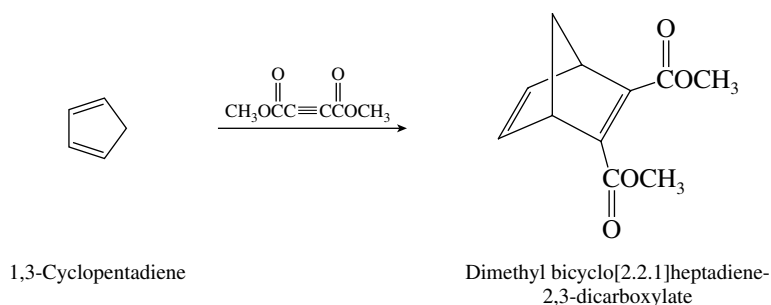
- (c) Nucleophilic substitution by cyanide converts the allylic bromide to 3-cyanocyclopentene.



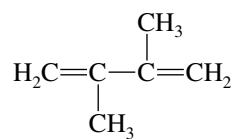
- (d) Reaction of the allylic bromide with a strong base will yield cyclopentadiene by an E2 elimination.



- (e) Cyclopentadiene formed in part (d) is needed in order to form the required Diels–Alder adduct.

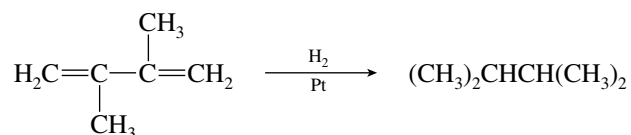


10.24 The starting material in all cases is 2,3-dimethyl-1,3-butadiene.

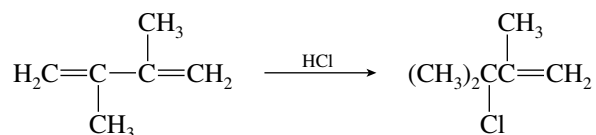


2,3-Dimethyl-1,3-butadiene

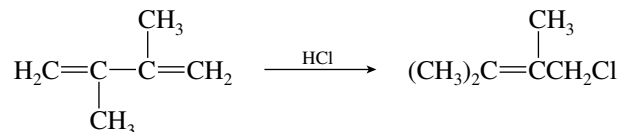
- (a) Hydrogenation of both double bonds will occur to yield 2,3-dimethylbutane.



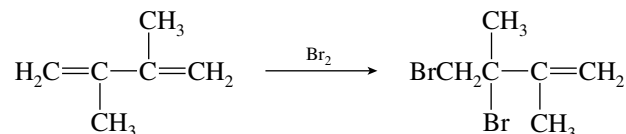
- (b) Direct addition of 1 mol of hydrogen chloride will give the product of Markovnikov addition to one of the double bonds, 3-chloro-2,3-dimethyl-1-butene.



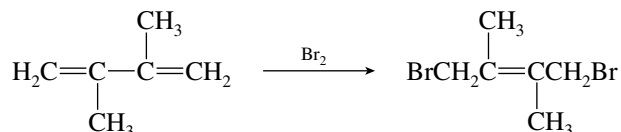
- (c) Conjugate addition will lead to double bond migration and produce 1-chloro-2,3-dimethyl-2-butene.



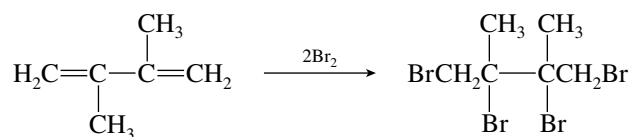
- (d) The direct addition product is 3,4-dibromo-2,3-dimethyl-1-butene.



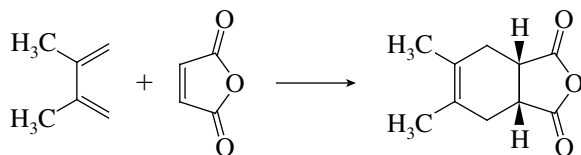
- (e) The conjugate addition product will be 1,4-dibromo-2,3-dimethyl-2-butene.



- (f) Bromination of both double bonds will lead to 1,2,3,4-tetrabromo-2,3-dimethylbutane irrespective of whether the first addition step occurs by direct or conjugate addition.



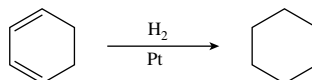
- (g) The reaction of a diene with maleic anhydride is a Diels–Alder reaction.



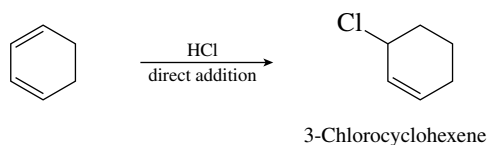
10.25 The starting material in all cases is 1,3-cyclohexadiene.



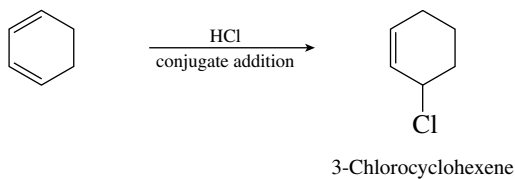
- (a) Cyclohexane will be the product of hydrogenation of 1,3-cyclohexadiene:



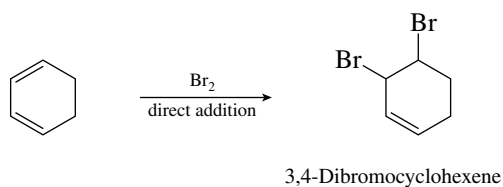
- (b) Direct addition will occur according to Markovnikov's rule to give 3-chlorocyclohexene



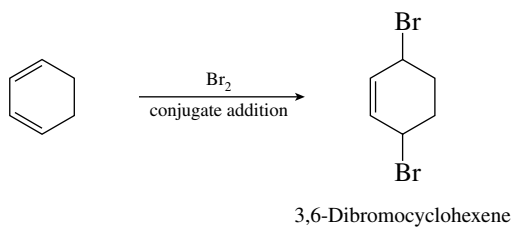
- (c) The product of conjugate addition is 3-chlorocyclohexene also. Direct addition and conjugate addition of hydrogen chloride to 1,3-cyclohexadiene give the same product.



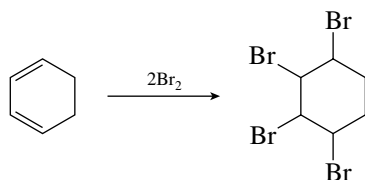
- (d) Bromine can add directly to one of the double bonds to give 3,4-dibromocyclohexene:



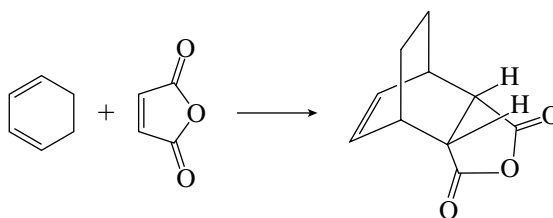
- (e) Conjugate addition of bromine will give 3,6-dibromocyclohexene:



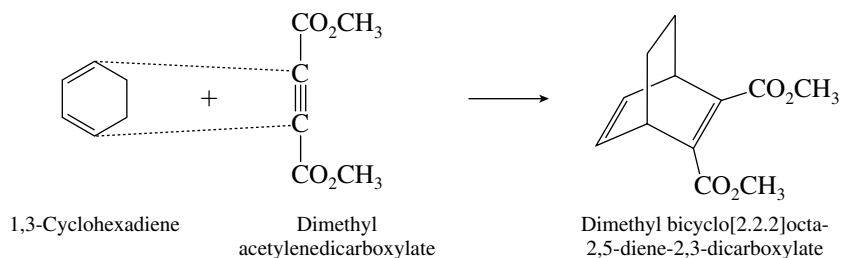
- (f) Addition of 2 moles of bromine will yield 1,2,3,4-tetrabromocyclohexane.



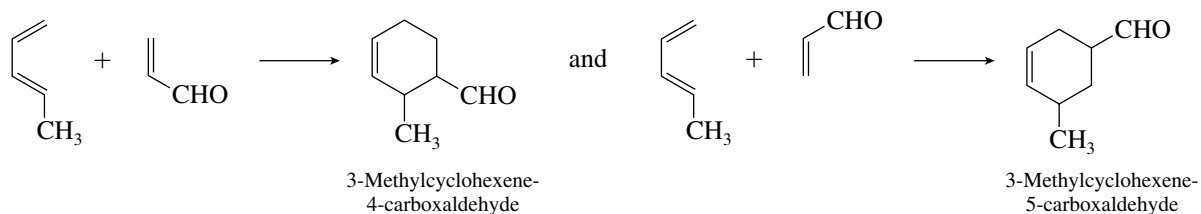
- (g) The constitution of the Diels–Alder adduct of 1,3-cyclohexadiene and maleic anhydride will have a bicyclo [2.2.2]octyl carbon skeleton.



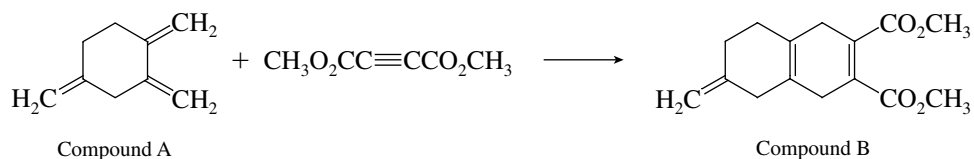
- 10.26 Bond formation takes place at the end of the diene system to give a bridged bicyclic ring system.



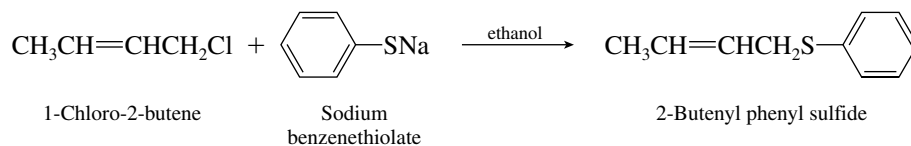
- 10.27 The two Diels–Alder adducts formed in the reaction of 1,3-pentadiene with acrolein arise by the two alignments shown:



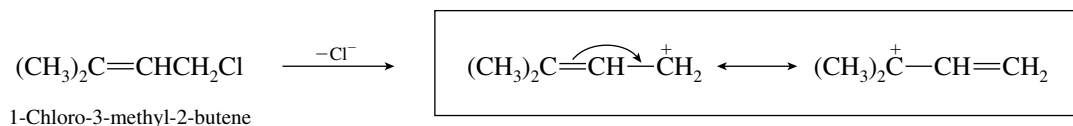
- 10.28 Compound B arises by way of a Diels–Alder reaction between compound A and dimethyl acetylenedicarboxylate. Compound A must therefore have a conjugated diene system.



- 10.29 The reaction is a nucleophilic substitution in which the nucleophile ($\text{C}_6\text{H}_5\text{S}^-$) becomes attached to the carbon that bore the chloride leaving group. Allylic rearrangement is not observed; therefore, it is reasonable to conclude that an allylic carbocation is *not* involved. The mechanism is $\text{S}_{\text{N}}2$.

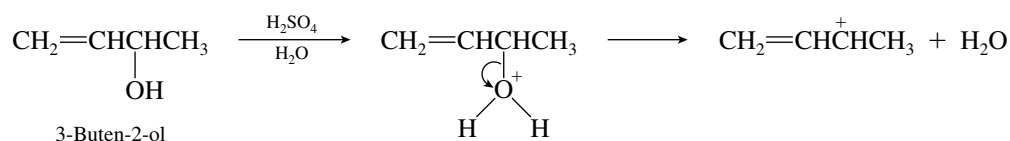


- 10.30 (a) Solvolysis of $(\text{CH}_3)_2\text{C}=\text{CHCH}_2\text{Cl}$ in ethanol proceeds by an $\text{S}_{\text{N}}1$ mechanism and involves a carbocation intermediate.

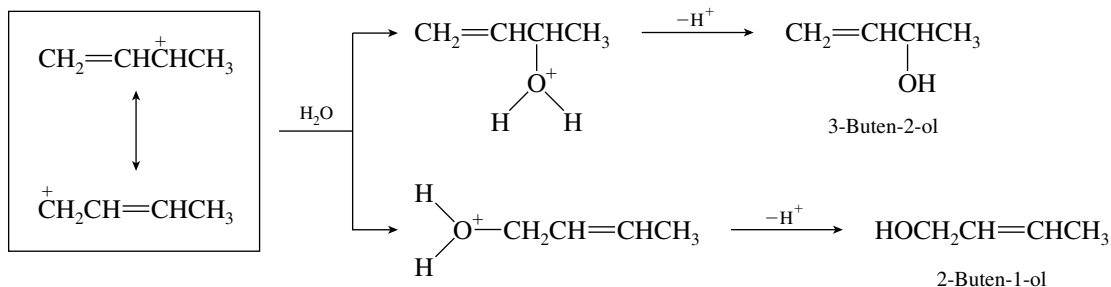


This carbocation has some of the character of a tertiary carbocation. It is more stable and is therefore formed faster than allylic cation, $\text{CH}_2=\overset{\oplus}{\text{C}}\text{HCH}_2$.

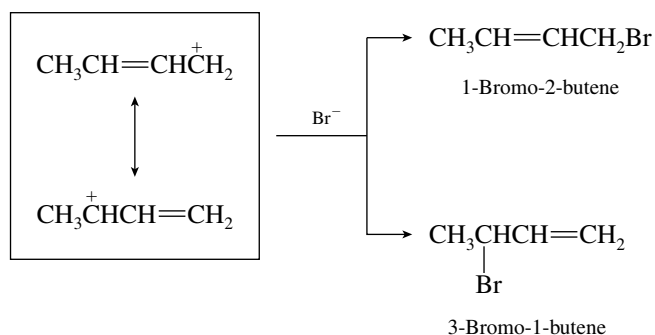
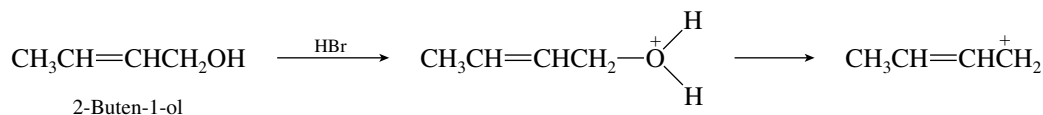
- (b) An allylic carbocation is formed from the alcohol in the presence of an acid catalyst.



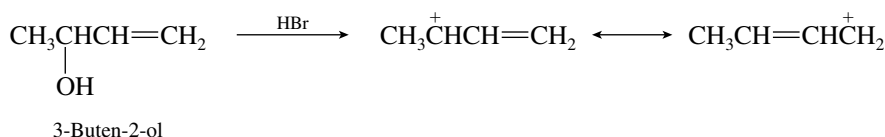
This carbocation is a delocalized one and can be captured at either end of the allylic system by water acting as a nucleophile.



- (c) Hydrogen bromide converts the alcohol to an allylic carbocation. Bromide ion captures this carbocation at either end of the delocalized allylic system.

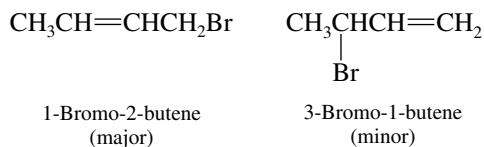


- (d) The same delocalized carbocation is formed from 3-buten-2-ol as from 2-buten-1-ol.



Since this carbocation is the same as the one formed in part (c), it gives the same mixture of products when it reacts with bromide.

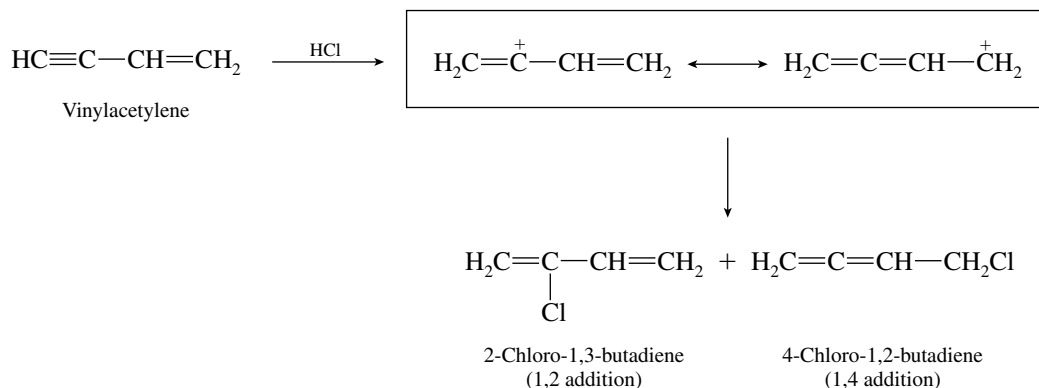
- (e) We are told that the major product is 1-bromo-2-butene, not 3-bromo-1-butene.



The major product is the more stable one. It is a primary rather than a secondary halide and contains a more substituted double bond. The reaction is therefore governed by thermodynamic (equilibrium) control.

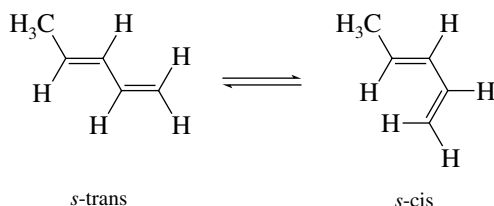
- 10.31** Since both products of reaction of hydrogen chloride with vinylacetylene are chloro-substituted dienes, the first step in addition must involve the triple bond. The carbocation produced is an allylic

vinyl cation for which two Lewis structures may be written. Capture of this cation gives the products of 1,2 and 1,4 addition. The 1,2 addition product is more stable because of its conjugated system. The observations of the experiment tell us that the 1,4 addition product is formed faster, although we could not have predicted that.

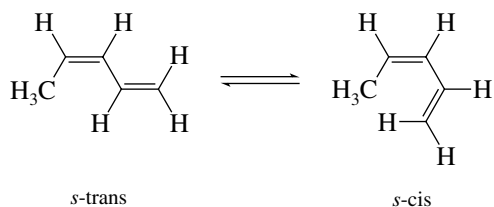


10.32 (a) The two equilibria are:

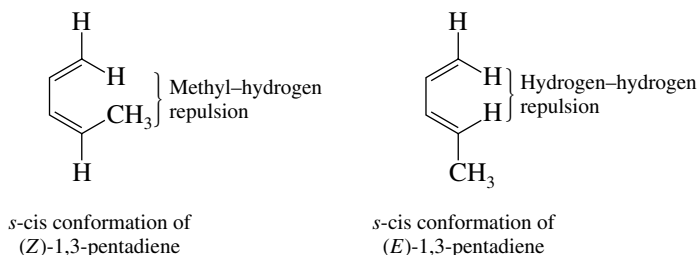
For (*E*)-1,3-pentadiene:



For (*Z*)-1,3-pentadiene:



(b) The *s*-cis conformation of (*Z*)-1,3-pentadiene is destabilized by van der Waals strain involving the methyl group.

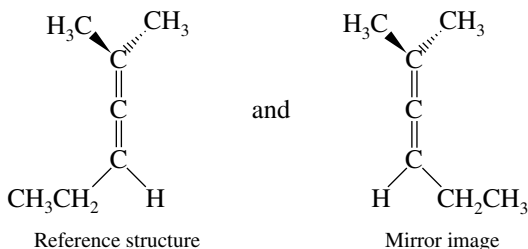


The equilibrium favors the *s*-trans conformation of (*Z*)-1,3-pentadiene more than it does that of the *E* isomer because the *s*-cis conformation of the *Z* isomer has more van der Waals strain.

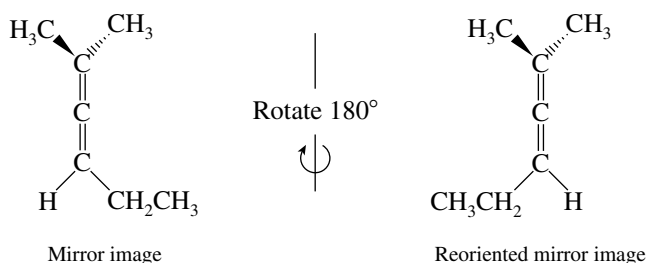
10.33 Compare the mirror-image forms of each compound for superposability.

(a)

2-Methyl-2,3-hexadiene

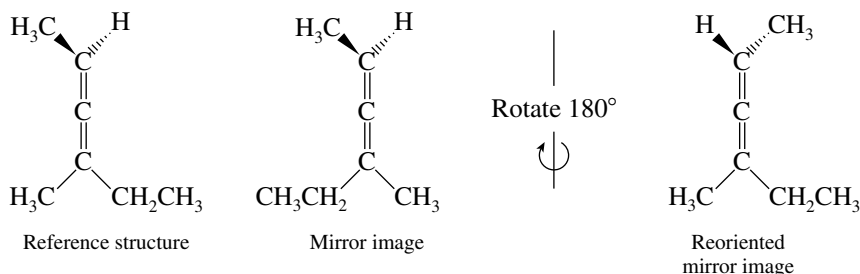


Rotation of the mirror image 180° around an axis passing through the three carbons of the $C=C=C$ unit demonstrates that the reference structure and its mirror image are superposable.



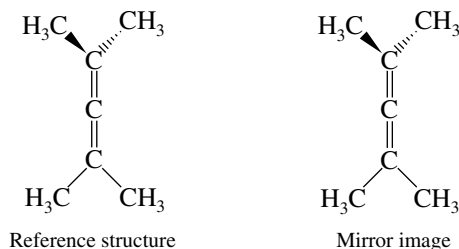
2-Methyl-2,3-hexadiene is an achiral allene.

(b) The two mirror-image forms of 4-methyl-2,3-hexadiene are as shown:



The two structures cannot be superposed. 4-Methyl-2,3-hexadiene is chiral. Rotation of either representation 180° around an axis that passes through the three carbons of the $C=C=C$ unit leads to superposition of the groups at the "bottom" carbon but not at the "top."

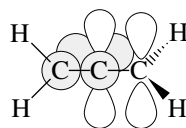
(c) 2,4-Dimethyl-2,3-pentadiene is achiral. Its two mirror-image forms are superposable.



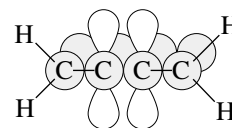
The molecule has two planes of symmetry defined by the three carbons of each CH_3CCH_3 unit.

10.34 (a) Carbons 2 and 3 of 1,2,3-butatriene are *sp*-hybridized, and the bonding is an extended version of that seen in allene. Allene is nonplanar; its two CH_2 units must be in perpendicular planes in order to maximize overlap with the two mutually perpendicular *p* orbitals at C-2. With one

more *sp*-hybridized carbon, 1,2,3-butatriene has an “extra turn” in its carbon chain, making the molecule **planar**.

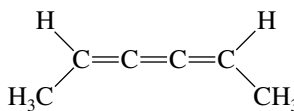
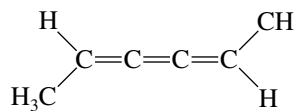


Nonplanar geometry of allene

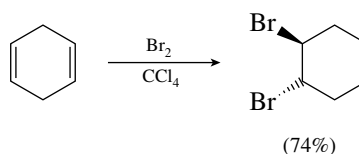


All atoms of 1,2,3-butatriene lie in same plane.

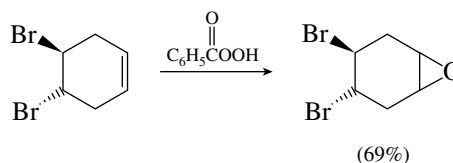
- (b) The planar geometry of the cumulated triene system leads to the situation where *cis* and *trans* stereoisomers are possible for 2,3,4-hexatriene ($\text{CH}_3\text{CH}=\text{C}=\text{C}=\text{CHCH}_3$). *Cis*–*trans* stereoisomers are diastereomers of each other.

*cis*-2,3,4-Hexatriene*trans*-2,3,4-Hexatriene

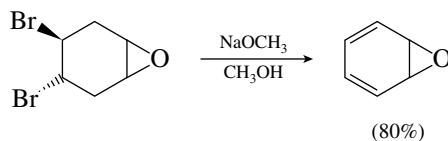
- 10.35** Reaction (a) is an electrophilic addition of bromine to an alkene; the appropriate reagent is **bromine in carbon tetrachloride**.



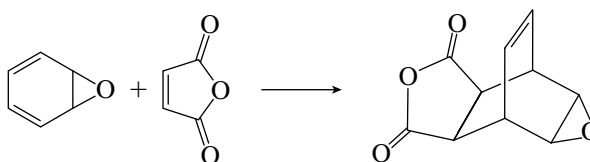
- Reaction (b) is an epoxidation of an alkene, for which almost any peroxy acid could be used. **Peroxybenzoic acid** was actually used.



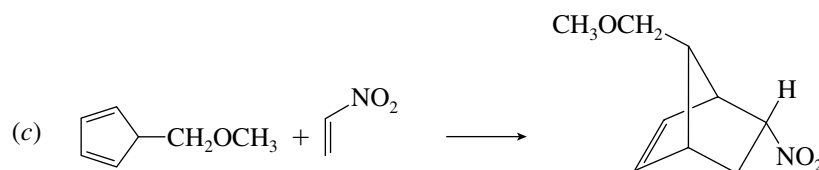
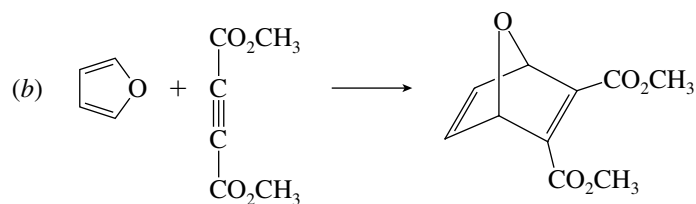
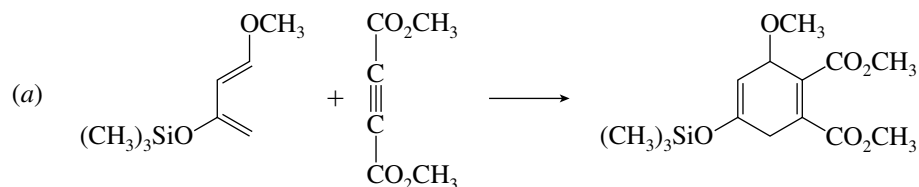
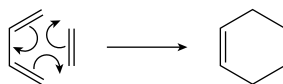
- Reaction (c) is an elimination reaction of a vicinal dibromide to give a conjugated diene and requires E2 conditions. **Sodium methoxide in methanol** was used.



- Reaction (d) is a Diels–Alder reaction in which the dienophile is **maleic anhydride**. The dienophile adds from the side opposite that of the epoxide ring.

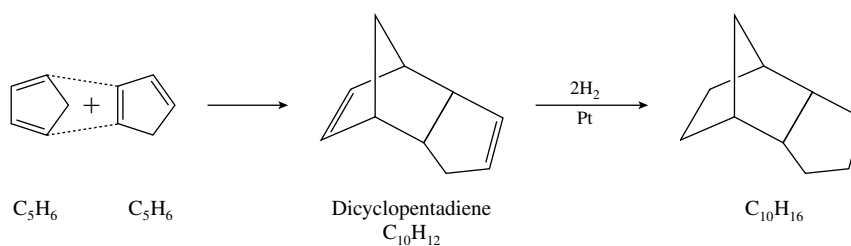


- 10.36** To predict the constitution of the Diels–Alder adducts, we can ignore the substituents and simply remember that the fundamental process is



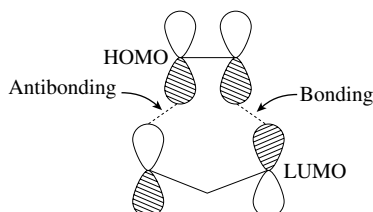
- 10.37** The carbon skeleton of dicyclopentadiene must be the same as that of its hydrogenation product, and dicyclopentadiene must contain two double bonds, since 2 mol of hydrogen are consumed in its hydrogenation ($C_{10}H_{12} \longrightarrow C_{10}H_{16}$).

The molecular formula of dicyclopentadiene ($C_{10}H_{12}$) is twice that of 1,3-cyclopentadiene (C_5H_6), and its carbon skeleton suggests that 1,3-cyclopentadiene is undergoing a Diels–Alder reaction with itself. Therefore:



One molecule of 1,3-cyclopentadiene acts as the diene, and the other acts as the dienophile in this Diels–Alder reaction.

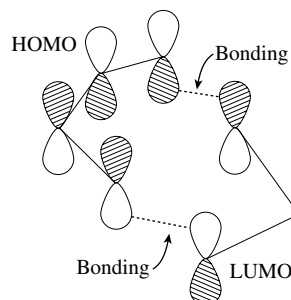
- 10.38** (a) Since allyl cation is positively charged, examine the process in which electrons “flow” from the HOMO of ethylene to the LUMO of allyl cation.



This reaction is forbidden. The symmetries of the orbitals are such that one interaction is bonding and the other is antibonding.

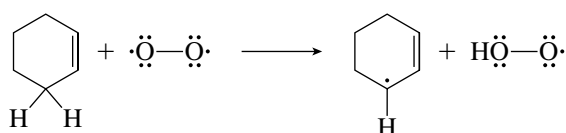
The same answer is obtained if the HOMO of allyl cation and the LUMO of ethylene are examined.

- (b) In this part of the exercise we consider the LUMO of allyl cation and the HOMO of 1,3-butadiene.

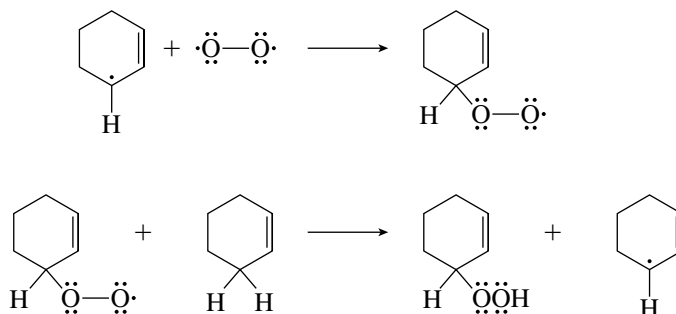


This reaction is allowed by the Woodward–Hoffmann rules. Both interactions are bonding. The same prediction would be arrived at if the HOMO of allyl cation and LUMO of 1,3-butadiene were the orbitals considered.

- 10.39** Since oxygen has two unpaired electrons, it can abstract a hydrogen atom from the allylic position of cyclohexene to give a free-radical intermediate.



The cyclohexenyl radical is resonance-stabilized. It reacts further via the following two propagation steps:



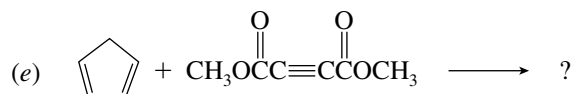
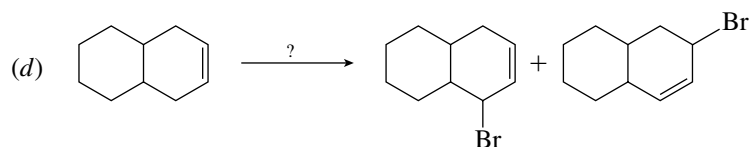
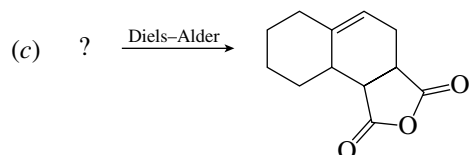
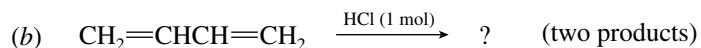
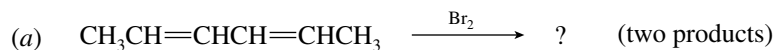
- 10.40–10.41** Solutions to molecular modeling exercises are not provided in this *Study Guide and Solutions Manual*. You should use *Learning By Modeling* for these exercises.

SELF-TEST

PART A

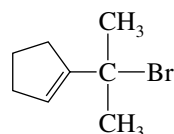
- A-1.** Give the structures of all the constitutionally isomeric alkadienes of molecular formula C_5H_8 . Indicate which are conjugated and which are allenes.
- A-2.** Provide the IUPAC name for each of the conjugated dienes of the previous problem, *including stereoisomers*.
- A-3.** Hydrolysis of 3-bromo-3-methylcyclohexene yields two isomeric alcohols. Draw their structures and the structure of the intermediate that leads to their formation.

A-4. Give the chemical structure of the reactant, reagent, or product omitted from each of the following:

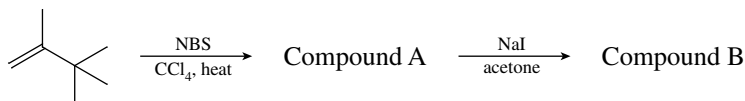


A-5. One of the isomeric conjugated dienes having the formula C_6H_8 is not able to react with a dienophile in a Diels-Alder reaction. Draw the structure of this compound.

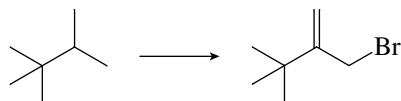
A-6. Draw the structure of the carbocation formed on ionization of the compound shown. A constitutional isomer of this compound gives the same carbocation; draw its structure.



A-7. Give the structures of compounds A and B in the following reaction scheme.



A-8. Give the reagents necessary to carry out the following conversion. Note that more than one reaction step is necessary.

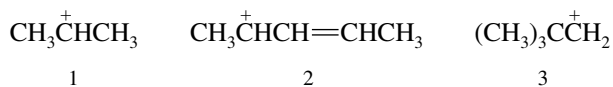


PART B

B-1. 2,3-Pentadiene, $\text{CH}_3\text{CH}=\text{C}=\text{CHCH}_3$, is

- A planar substance
- An allene
- A conjugated diene
- A substance capable of cis-trans isomerism

B-2. Rank the following carbocations in order of increasing stability (least \rightarrow most):

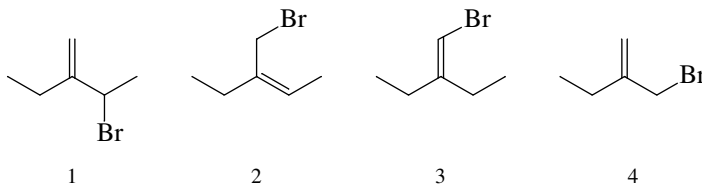


- (a) $1 < 2 < 3$ (c) $3 < 1 < 2$
 (b) $2 < 3 < 1$ (d) $2 < 1 < 3$

B-3. Hydrogenation of cyclohexene releases 120 kJ/mol (28.6 kcal/mol) of heat. Which of the following most likely represents the observed heat of hydrogenation of 1,3-cyclohexadiene?

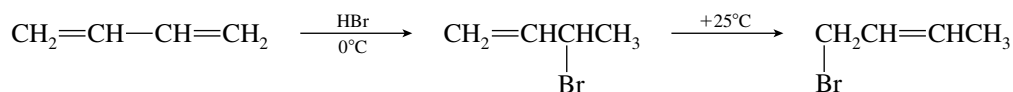
- (a) 232 kJ/mol (55.4 kcal/mol)
 (b) 240 kJ/mol (57.2 kcal/mol)
 (c) 247 kJ/mol (59.0 kcal/mol)
 (d) 120 kJ/mol (28.6 kcal/mol)

B-4. Which of the following compounds give the *same* carbocation on ionization?



- (a) 1 and 3 (c) 1 and 2
 (b) 2 and 4 (d) 1 and 4

B-5. For the following reactions the major products are shown:



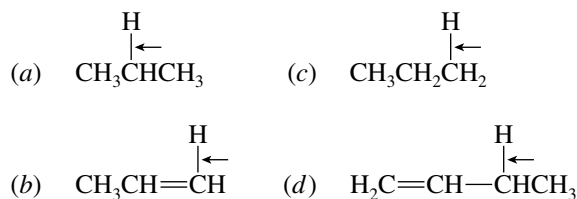
These provide an example of 1 control at low temperature and 2 control at higher temperature.

1

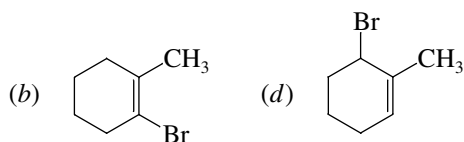
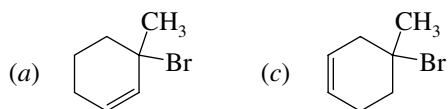
2

- (a) kinetic thermodynamic
 (b) thermodynamic kinetic
 (c) kinetic kinetic
 (d) thermodynamic thermodynamic

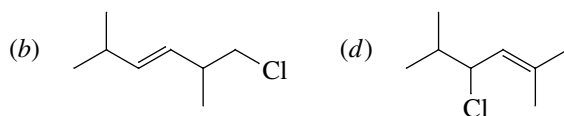
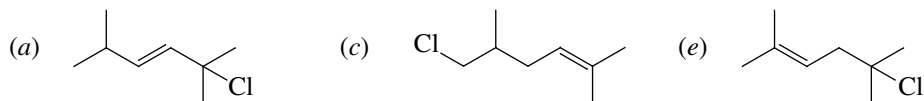
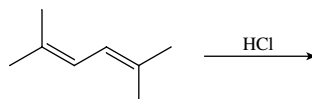
B-6. Which of the following C—H bonds would have the smallest bond dissociation energy?



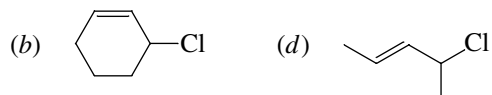
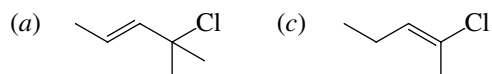
B-7. Which of the following compounds would undergo solvolysis (S_N1) most rapidly in aqueous ethanol?



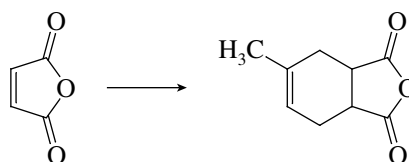
B-8. What is the product of 1,4-addition in the reaction shown?



B-9. Which of the following compounds will undergo hydrolysis (S_N1) to give a mixture of two alcohols that are constitutional isomers?



B-10. What hydrocarbon reacts with the compound shown (on heating) to give the indicated product?



- (a) 2-Methyl-1-butene (d) 2-Methyl-1,3-butadiene
 (b) 2-Methyl-2-butene (e) 1,3-Pentadiene
 (c) 3-Methyl-1-butyne